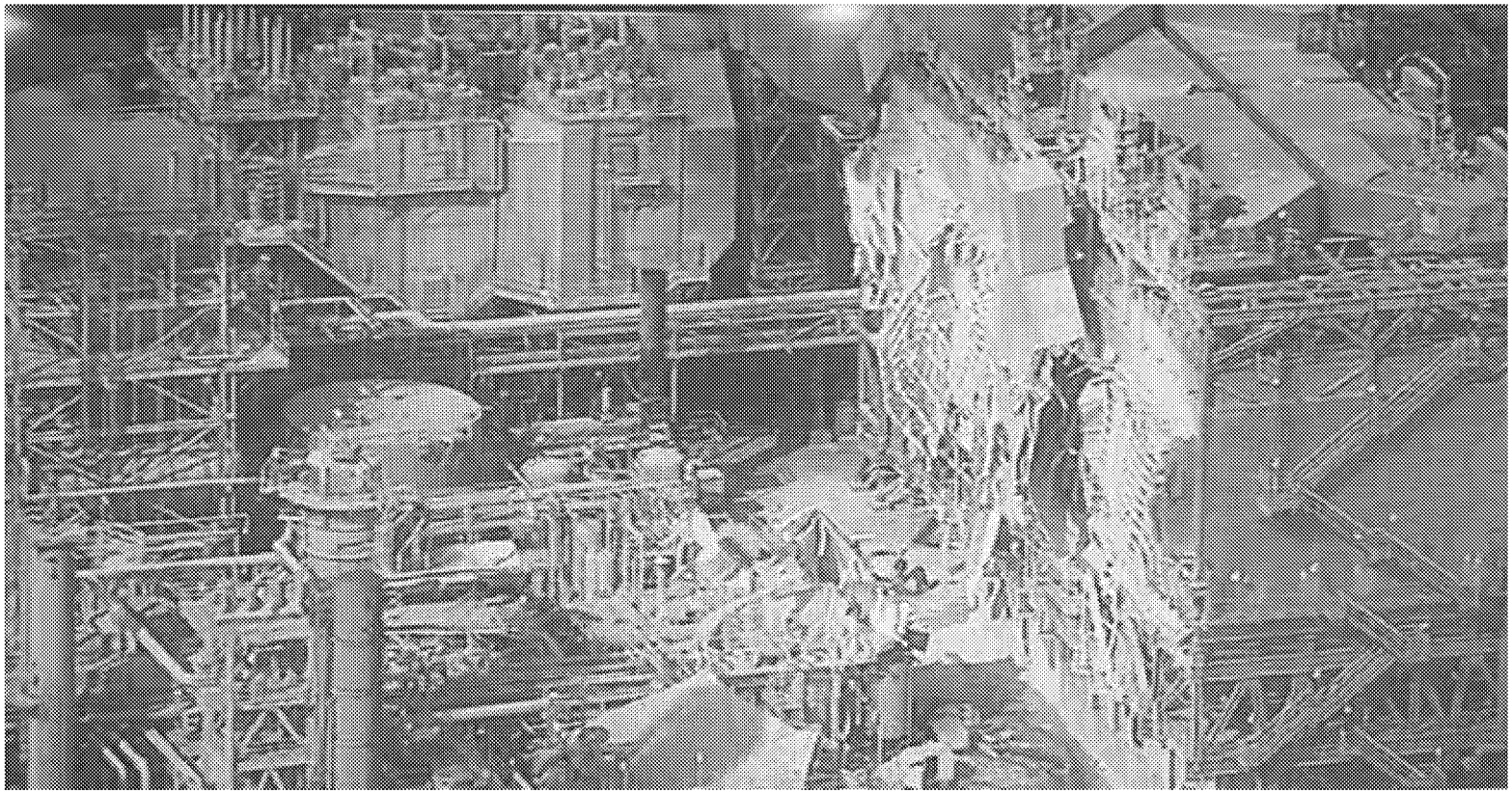
PUT WORKER AND COMMUNITY SAFETY FIRST



THIS IS NO PLACE FOR MODIFIED HYDROFLUORIC ACID

THE CASE AGAINST MHF

Sally Hayati, Ph.D. EE-CoE

Last updated: May 19, 2016

TORRANCE REFINERY ACTION ALLIANCE
PRIORITIZING COMMUNITY SAFETY

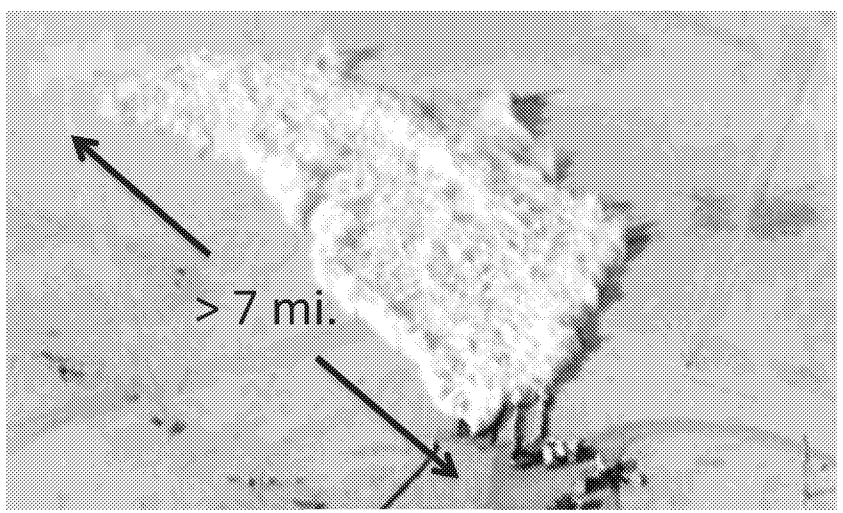
A RISK TOO GREAT

HYDROFLUORIC ACID IN U.S. REFINERIES

"No industrial process risks more lives from a single accident than does … alkylation using hydrogen fluoride in oil refining… Fortunately, [alternatives exist and] HF alkylation can be entirely eliminated. The industry has the technology and expertise. It certainly has the money. It lacks only the will. And if it cannot find the will voluntarily, ***it must be forced by government action***. This is truly a risk too great."

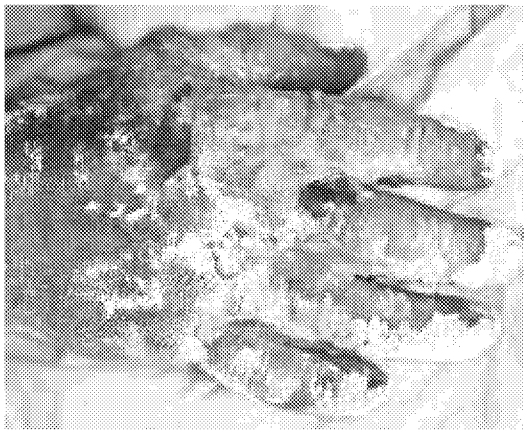
The United Steel Workers

- 1986 **HF** Release Tests (Goldfish)
- Nevada DOE test site
- 1,000-gal. (8,300 lb) **HF** released in 2 minutes (typical refinery conditions)
- 100% of HF became airborne
- Sensor measurements showed HF cloud lethal at 5 mi, immediately dangerous to life or health at 7.5 mi.



HF is Toxic

"Hydrofluoric Acid (HF) is an acid like no other… Even very strong acids don't have the power to cause death and injury the way HF can."



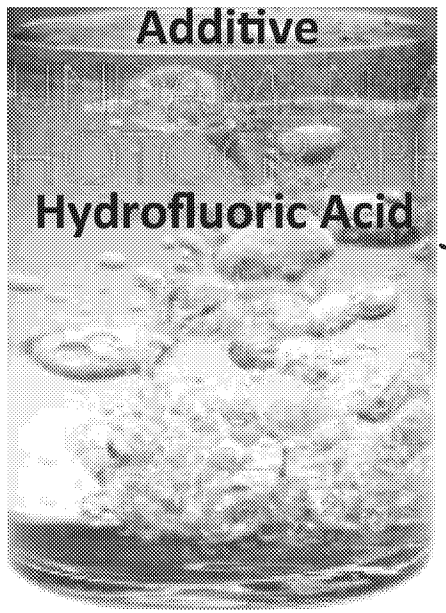
HF Burns

1. Corrosive burns from hydrogen ions (H^+)
   - Very corrosive, etches and reacts with metal, glass, concrete, ceramics, and stone
2. Chemical burns and systemic poisoning from Fluoride ions (F^{--})
   - Deep chemical burn, slow to heal, requires immediate HF-specific treatment
   - Fluoride ion penetrates tissues deeply, bonds w/ Calcium, causes local cellular destruction & systemic toxicity, readily absorbed through intact or damaged skin.
   - Low blood pressure, irregular heartbeat, involuntary muscle contractions, seizures.
   - Survivors may suffer: chronic lung disease, extensive scarring, bone loss, lasting visual defects, blindness, total eye destruction, persistent narrowing of esophagus
   - Prompt HF-specific treatment needed for even minor exposure: damage may progress for days before symptoms appear

In 1999 an "empty" HF container was compressed and burst in a garbage truck. A few drops of HF (70%) sprayed a NYC sanitation worker. Despite emergency care, he died of heart failure.

What is Modified Hydrofluoric Acid (MHF)?

- MHF= Hydrofluoric acid (HF) + vapor-suppressant **Additive** to reduce airborne HF
- **Airborne Reduction Factor (ARF)** measures how much less acid becomes airborne
- The higher the % additive concentration, the less HF will become airborne (the greater the ARF)
- But the additive interferes w/ alkylation, rendering MHF *unusable* at safer, higher additive concentrations
- History of false promises & additive concentration reduction: 50% additive (1990), 30% (1994), 10% (1998)
- The last reduction, to 10%, has been kept hidden from the public but was exposed by TRAA in Nov. 2015
- According to HF expert Dr. Ronald Koopman, with 10%-20% additive there is very little difference between HF and MHF.



Modified Hydrofluoric Acid

90% of released MHF becomes airborne in a dense, toxic HF cloud.

MHF Has Never Performed as Advertised

*-Mutating Consent Decree tracked MHF's **dwindling Airborne Reduction Factor (ARF)** -*

1990: **ARF=100%** MHF would not form a dense vapor cloud

- *Torrance-Mobil Consent Decree condition.* Otherwise Mobil must adopt sulfuric acid.
- 50% additive. The additive needs to be a least this high to make HF "safe."

1994: **ARF=65%** MHF forms a vapor cloud like HF does, but less than ½ the size

- Consent Decree changed by a *Stipulation & Order* to allow use of MHF anyway
- 30% additive. Mobil convinces the city that a "less deadly" HF is good enough.

MHF unit failed at start of operations, end of '97. 30% additive trashed the alky unit. Additive was secretly slashed & little barriers sprinkled over parts of the unit.

1998: **ARF ≈ 10%.** MHF forms a vapor cloud nearly the same size as HF (90%)

- Never revealed to public, approved by Chief R. S. Adams, Chief Hall, unknown others
- 10% additive. MHF is now 90% HF and barely less deadly.

Yet ExxonMobil & the City of Torrance still publicly make false safety claims

- MHF is viable and safe—ExxonMobil. MHF falls on the ground—City of Torrance
- They've been unchallenged because **the 1998 change has never been acknowledged**

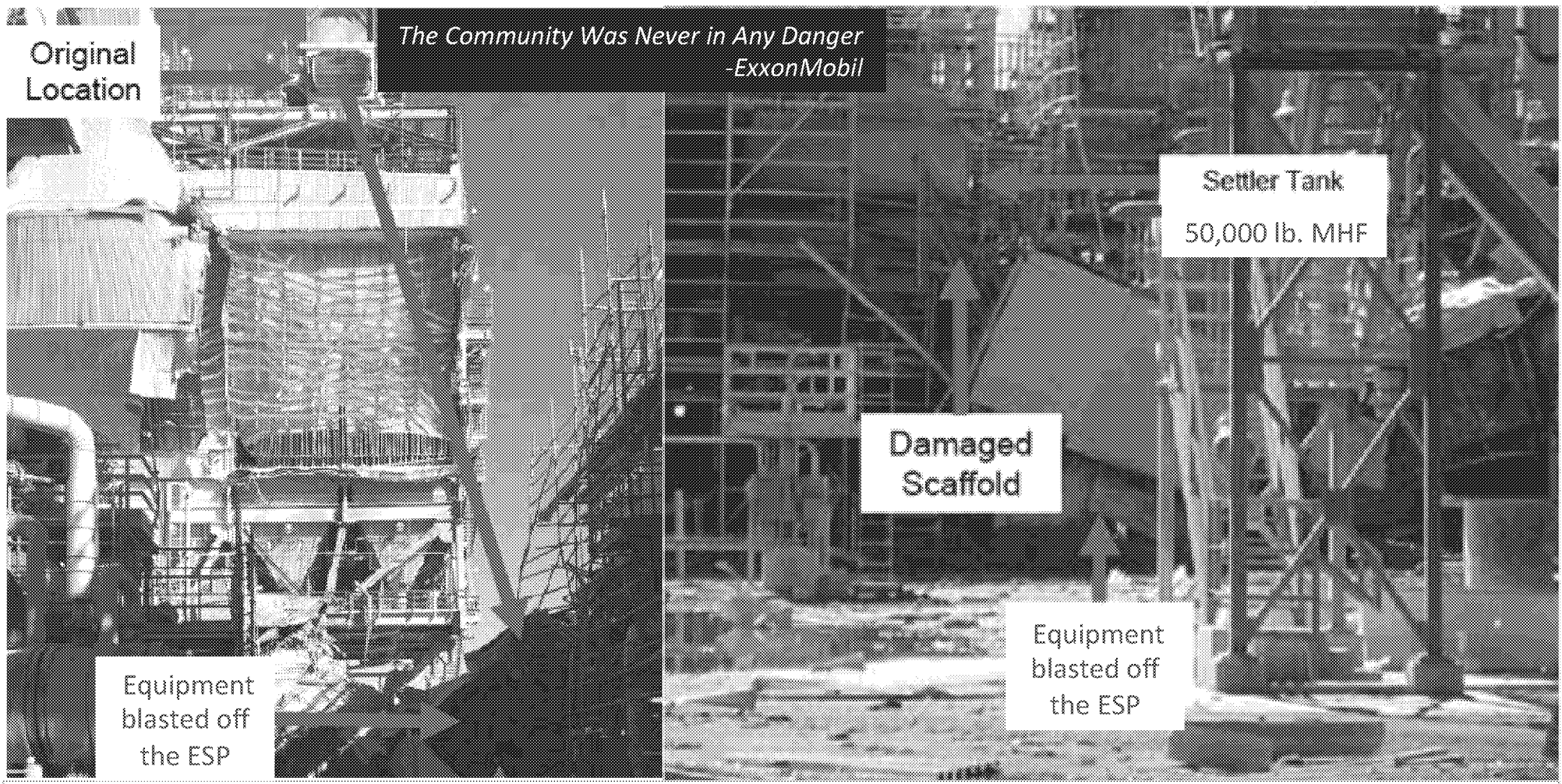
Myths Told About the "Safety" of MHF

JUST... TRUST

- No significant accidental release can happen because of layers of protection
  - It almost did happen: the 2/18/2015 accident was a near miss on a tank of 50K lb. MHF
- Emergency systems will keep us safe in case of any release
  - At best, emergency systems *may reduce but not eliminate* the impact of a release
  - If a release is large enough, it will impact the community even with emergency measures
  - Emergency measures may underperform or fail due to damage, negligence, or human error
- Earthquake damage can't cause a significant MHF release, due to seismic design
  - Even the Consent Decree Safety Advisor acknowledged in his 1995 report that a significant quake could release MHF while simultaneously making emergency equipment unusable
- There is no alternative
  - More than half US alky units use sulfuric acid alkylation, which poses no offsite toxic risk
  - At least one new safer technology is ready for commercialization: solid acid catalyst
  - If no alternative is acceptable to the refinery, alkylation could be eliminated
- Terrorist attacks can be prevented by keeping details on MHF a secret
  - Terrorists don't need the MHF details; they have all the info they need about its HF nature
- You can trust ExxonMobil. They designed and will maintain MHF to keep us safe.
  - They put profits before safety, secretly reducing the additive below any useful concentration
  - They hide info the public needs to understand MHF risks behind false trade secret claims, even though Honeywell has a MHF monopoly and most "trade secrets" are available online

A Catastrophic Accident Nearly Happened during Torrance Explosion

-Chemical Safety Board says the Feb. 18, 2015 explosion was a near miss on MHF tank-



An 80,000 lb. duct sent flying by the explosion landed 3 ft. from settler tank in the **ALKLATION UNIT**. Vanessa Sutherland, Chemical Safety Board (CSB) Chair: "We were really, really lucky... [This was] a near miss … It could have been much more catastrophic… … If I were in the community I absolutely would be concerned." The Torrance refinery has 250,000 lb. MHF at the alkylation unit.

MHF is TOO HIGH A RISK for a Dense Urban Area

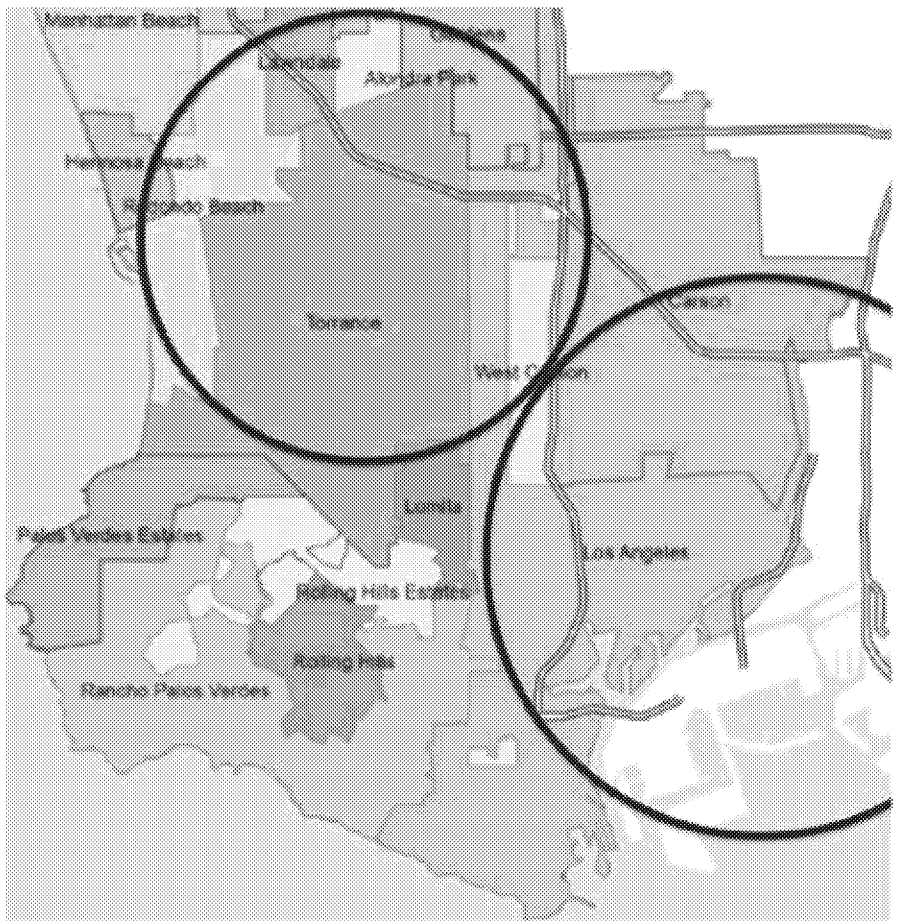
-Even if every proprietary and unverified industry claim were the gospel truth-

Official scenario maps from Valero Wilmington & ExxonMobil Torrance EPA Offsite Consequence reports

615,524 residents within these zones are at risk of death (closer to each refinery), or irreversible and serious health effects from short-term exposure if these accidents occur. *Actual exposure depends on wind direction*.

Torrance, Redondo Beach, Lawndale, Gardena, Carson, Manhattan Beach, Hermosa Beach, West Carson, Los Angeles, Lomita, Long Beach, Hawthorne

BUT **Industry data have been found online that show these "official" risk zone areas are *very significantly understated*.**



The Beautiful South Bay

Livable Cities, or Sacrifice Zone?

XOM's EPA Report Falsely Minimizes Risk

EPA Risk Management Program (RMP) offsite consequence analysis (OCA) worst case scenario (WCS)

- Facilities using a federally regulated substance over a threshold amount must submit a report
- MHF is a federally regulated substance in amounts over 1,000 lb. ExxonMobil has 250,000 lb.
- Worst-case scenario: a calm night, failure of *active* mitigation measures like water suppression systems, the release, over 10 minutes, of *the largest quantity of MHF contained in a single vessel or process line*.
- Two aspects of ExxonMobil's EPA report are questionable
  - 70% Airborne Reduction Factor (ARF) or close to it used by EM. For a 10% additive, *ARF = 10%*
  - 5,200 lb. MHF released. But the *largest amount MHF contained in a single vessel is 50,000 lb.*
    - The Mobil Torrance Refinery 1999 EPA RMP WCS: 50,000 lb. MHF in the settler
    - The City of Torrance Staff Report, October 13, 2015: 50,000 lb. MHF in each of 2 settlers

ExxonMobil's chosen scenario:	5,200 lb. MHF	~70% ARF	3.2 mi. radius
What we believe it should be:	50,000 lb. MHF	≤26% ARF	≥ 13.7 mi. radius

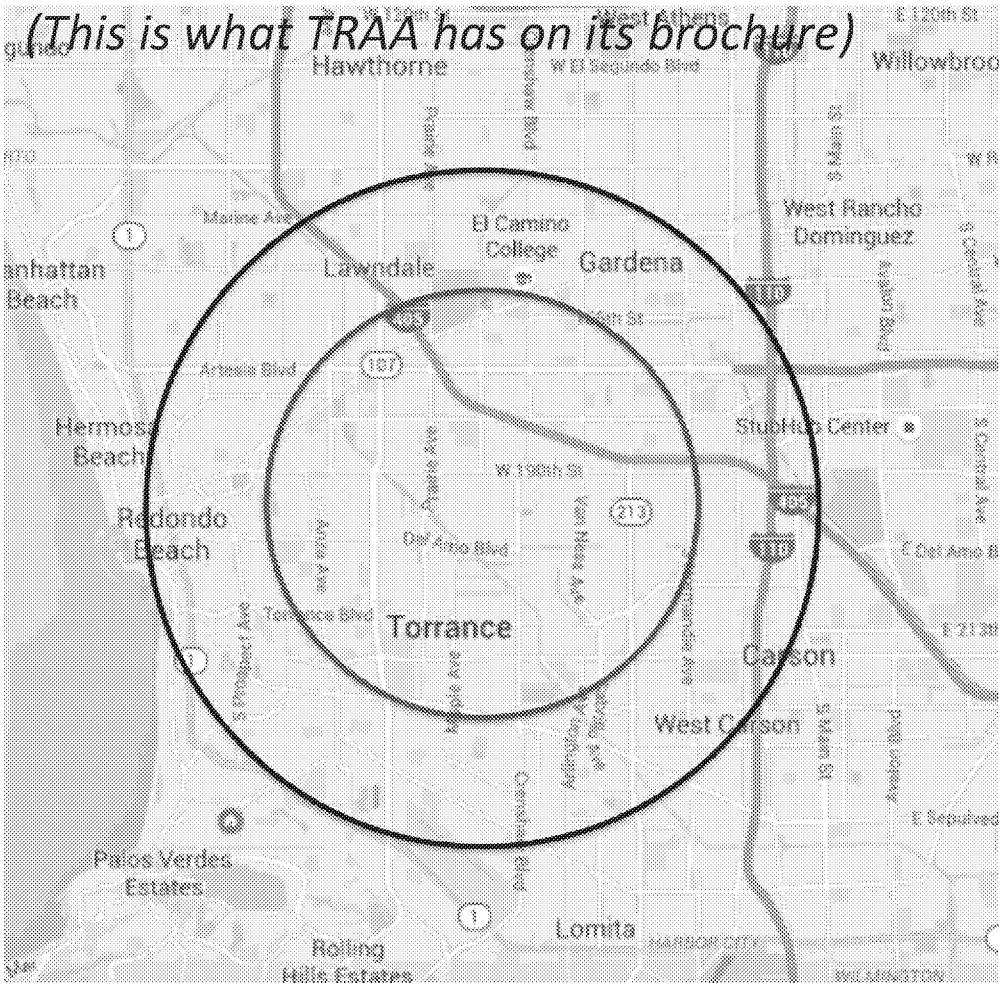
The following 2 slides should what EM's worst case scenario would look like

(1) for the same release assuming 20% ARF, (2) for a 50,000 lb. release w/ 20% ARF

Scenario Maps for Different Airborne Reduction Factors (ARF)

***-5,200 lb. MHF release** for a 65% ARF (L) vs. 26% ARF (R)*

(This is what TRAA has on its brochure)



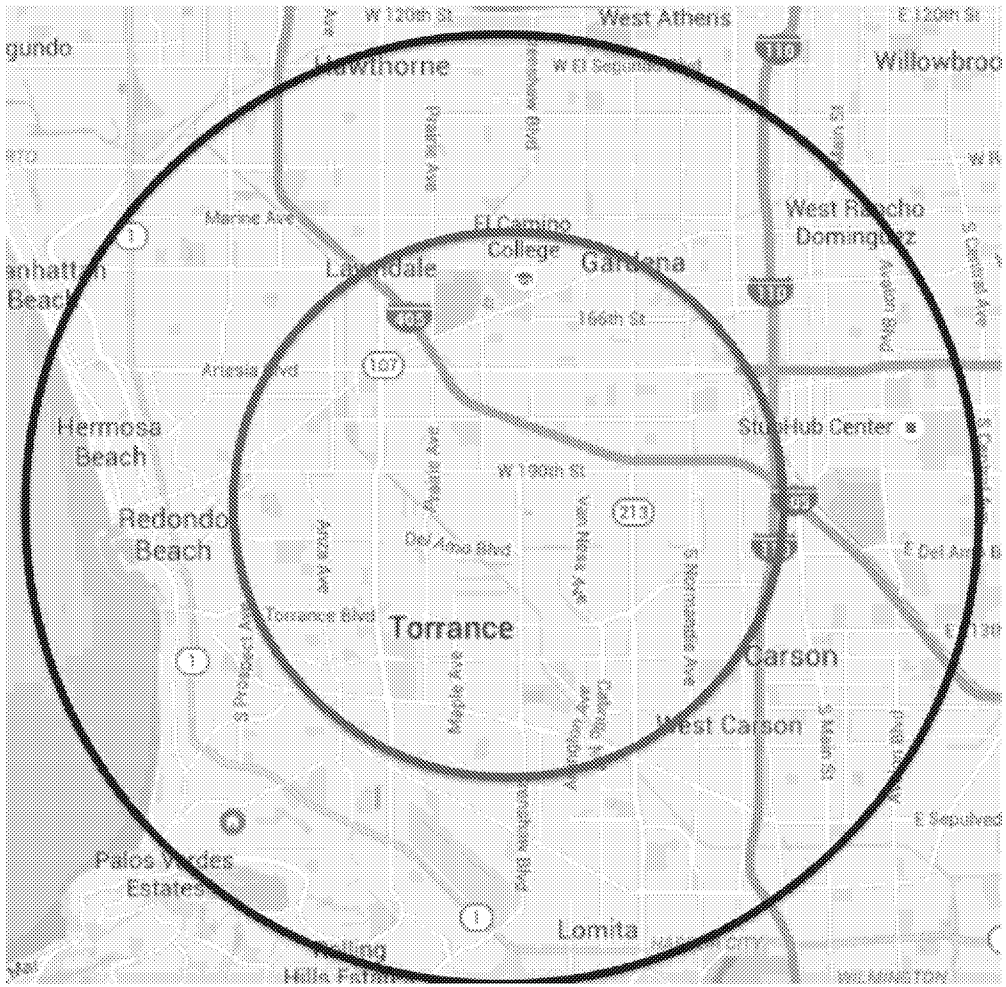
ExxonMobil's EPA MHF "worst-case" scenario

2 mi radius death zone, 3.2 mi serious & irreversible injury.

5,200 lb. released in 10 min. ARF: *70% or close to it.*

Giving an "effective" HF release rate of 150 lb./min.

(Death radius (>ERPG-3) estimated by TRAA)



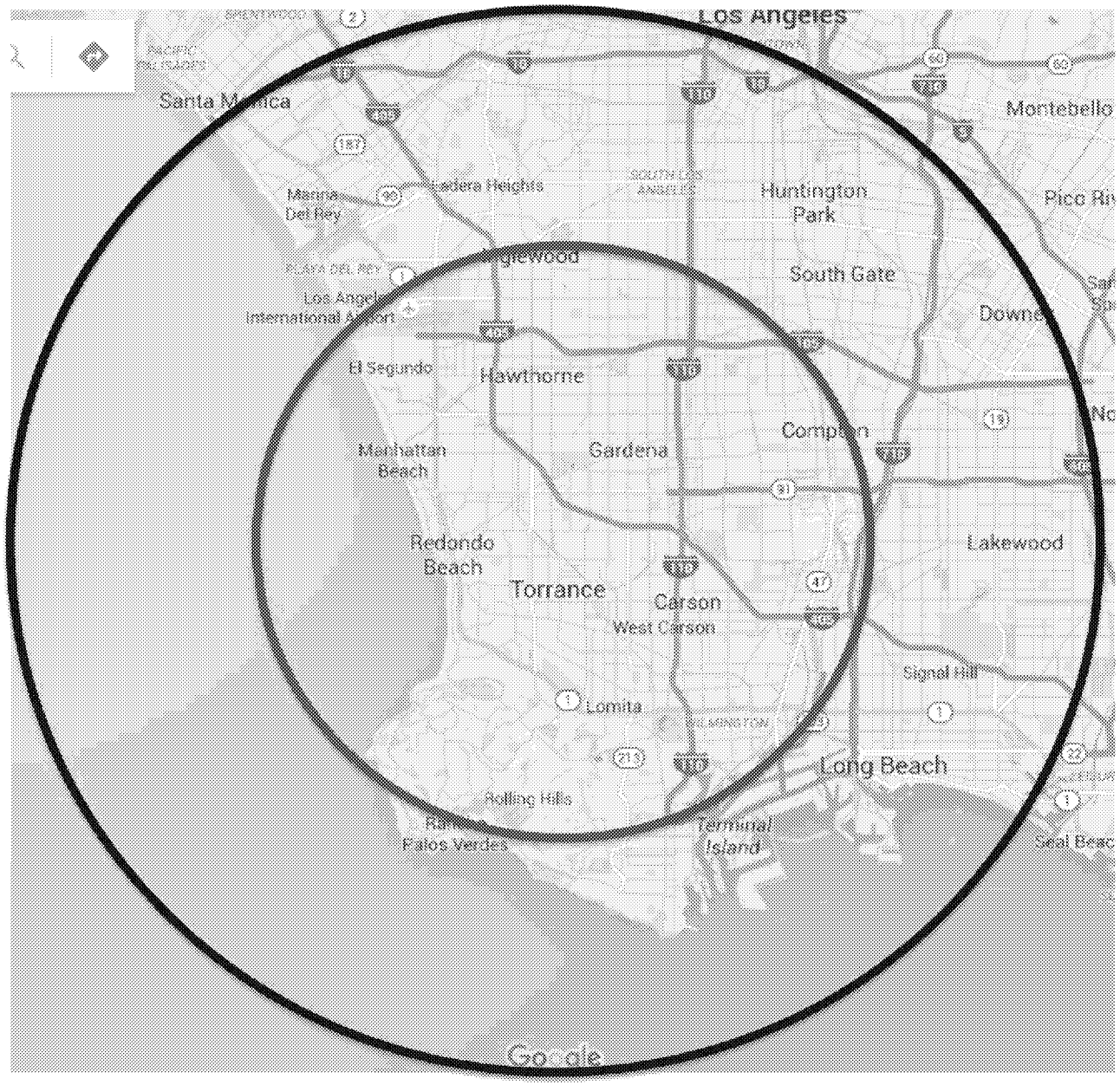
The same accident, with ARF=26%. 2.8 mi radius death zone, 4.6 mi serious & irreversible injury

5,200 lb. released in 10 min. ARF: 26%.

Giving an "effective" HF release rate of 385 lb./min.

The 2/18/2015 Near-Miss Could have Been This Bad

-50,000 lb. MHF release scenario map, assuming EPA worst-case conditions-



Torrance Refinery Release of 50,000 lb. MHF from acid settler, calm day, No active mitigation, urban conditions, 26% ARF

Effective HF Release rate: 3,700 lb./min. over 10 min, gives 37,000 lb. airborne HF

13.7 mi. radius zone (black) of serious & irreversible health effects for most with short term exposure (>20 ppm, ERPG-2)

7.7 mi. radius zone (red) life-threatening for most w/ short term exposure (> 50 ppm, ERPG-3)

Actual exposure to HF plume depends on wind direction

A Rough Sanity Check

-Could MHF possibly be that bad? Yes, it could.-

Scenario: 50,000 lb. MHF released over 10 min., w/ 26% MHF mitigation, **13.7 MI. TOXIC DISTANCE**

- *26% is generous*: evidence shows MHF w/ 10% additive reduces airborne acid by only ~10%

Compare that scenario to EPA reports from all 48 HF alkylation units in the US.

- Valero Wilmington's 2004 EIR stated MHF w/ 10% additive reduces HF toxic distance by 7.9%
- Median endpoint distance for HF worst-case scenarios = 15 miles
  - The median refinery HF inventory is 150,000 lb. Torrance has 250,000 lb and Valero has 578,000 lb of MHF
- If all refineries switched to MHF, median endpoint distance would go from 15 mi. to ~ 13.8 mi.

Comparison to actual measurements taken during the Goldfish HF Release Test (table below)

- 4.5 times more airborne HF for our scenario than for Goldfish
- Our scenario has early the same release rate (90%) for 5 times longer than Goldfish
- Yet our toxic endpoint distance is only 1.8 times farther to a concentration (20 ppm) 50% lower than for Goldfish (30 ppm)

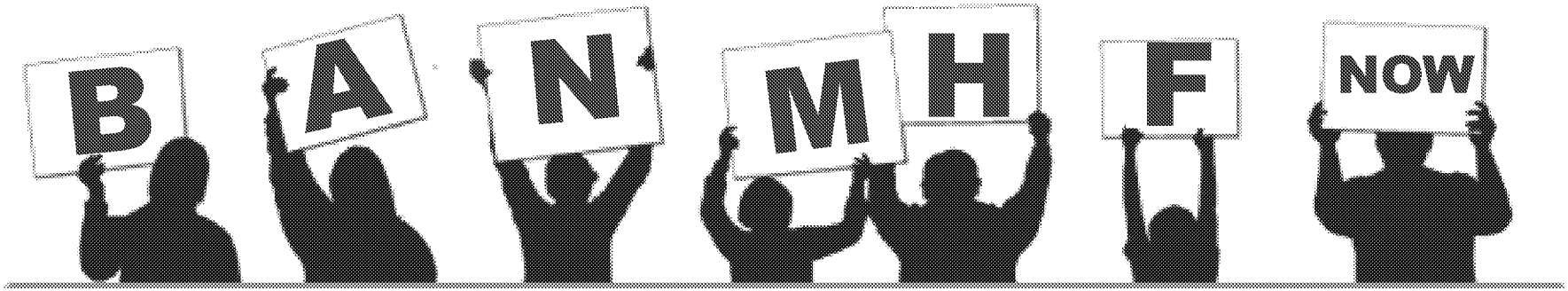
	Release Amount	Total HF Airborne	Release Time	Cloud Toxicity	At Distance
Goldfish measurements	8300 lb. HF	8300 lb.	2 min	30 ppm (IDHL)	7.5 mi.
Our scenario (Table 7)	50000 lb. MHF	37000 lb.	10 min	20 ppm (ERPG-2)	13.7 mi

Don't Let This Happen to the South Bay!

-BAN MHF in CA BEFORE IT'S TOO LATE-

Gumi, South Korea, 2012, 16,000 lb. HF released

5 dead, 12 hospitalized for up to 10 days, 12,243 treated for HF exposure, 1,000's *evacuated* for weeks, $20 million in immediate losses at 80 surrounding businesses. The area was declared a "special disaster zone." All this, even though *prevailing winds carried the HF cloud away from the city*.



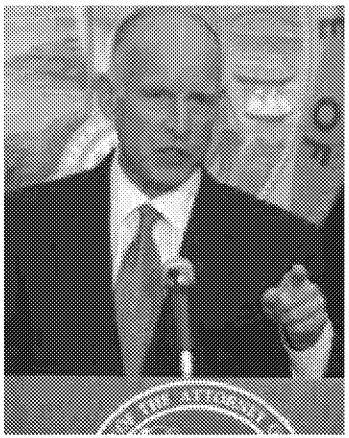
BEFORE AN ACCIDENT AT VALERO, WILMINGTON OR TORRANCE CAUSES A SOUTH BAY BHOPAL

- Technology alternatives to MHF: sulfuric acid and solid acid catalyst
- The state could pass a law banning HF/MHF at refineries
  - CA Assemblyman Bob Bonta's AB 1759 is parked in committee but could be resurrected & improved
- South Coast Air Quality Management District (SCAQMD) has the authority to ban it
  - Responded to TRAA demands for a ban with promises of a "study of alternatives."
- Cities of Torrance & LA could ban ≥ 1,000 lb. HF/MHF in urban areas (DHS limit)
- **South Bay communities must organize to demand a ban, or it won't happen**

SUGGESTIONS for ACTION:

1. Educate yourself and others about MHF: http://bit.ly/1T9hLXN
2. Join TRAA: Meetings 1st & 3rd Mondays, 6pm, Sizzler 2880 Sepulveda Blvd, Torr.
3. Sign the petition to ban MHF: http://chn.ge/1Wf1Hav
4. "Like" the Torrance Refinery Action Alliance Facebook page, share posts, comment
5. Pressure elected officials Hadley, Allen, & Hall, and the AQMD board to ban MHF.
6. Encourage clubs, groups, organizations. and school districts to oppose MHF
7. For more info: info@safetorrancerefinery.com

Against MHF



MHF [is] an extremely toxic and volatile compound that can pose a risk to the public health ... [E]liminat[ing] the use of hydrofluoric acid in any form, [would be] a very substantial benefit....the use of MHF should be avoided when...there is a viable alternative.

Office of (then) CA Attorney General Jerry Brown, 2008

[The] use [of] "modified HF acid" for alkylation is a strategy that I oppose vigorously. This is an approach the majority of the refining industry does not use. There have been good options from the beginning [namely, sulfuric acid] ...There are those in the industry that cling to their belief in "modified HF acid" and the supporting technology. Most of those advocates either sell the design or license it. ...When all else fails, the advocates for such a strategy resort to the claim that...the two acids are equally safe."

Donald Hall, former refinery manager for the Big West in Bakersfield & Texaco's Los Angeles plant, 2008

[The February 18 explosion at the Torrance Refinery was a] "near miss" [on the MHF tank.] "It could have been much more catastrophic... If I were in the community I absolutely would be concerned."

Vanessa Sutherland, Chemical Safety Board Chair, 2015.